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Spectrophotometric Determination of Nickel after Separation by Collection of its APDC Complex on Microcrystalline Naphthalene

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A method is described for the spectrophotometric determination of trace amounts of nickel after separation by collection of its APDC complex on microcrystalline naphthalene. APDC reacts with nickel to form a water-insoluble complex, which is easily collected on microcrystalline naphthalene, and the resulting mixture of the complex and naphthalene is separated from the aqueous solution and dissolved in dimethylformamide. The absorbance of the solution is measured at 379 nm to determine the trace amounts of nickel. The various factors such as pH, amounts of reagent and naphthalene, shaking time standing time and diverse ions are studied.

1 Introduction

Ammonium Pyrrolidinedithiocarbamate(APDC) forms water-insoluble complexes with various metal ions such as Cu, Co, Bi, Ni, Mn, etc.. These complexes are easily extracted into molten naphthalene or chloroform under the optimum conditions. In this communication, a APDC was chosen as a useful complexing reagent for the spectrophotometric determination of trace nickel. This complexing reagent reacts with nickel in the pH range 1.2-10.2 with the formation of a water-insoluble complex, which is quantitatively collected on microcrystalline naphthalene at room temperature. The mixture of the complex and naphthalene separated from the aqueous solution and dissolved in dimethylformamide. The absorbance of the solution is measured at 379 nm against the reagent blank. The trace amounts of nickel is determined from a calibration curve.

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2 Experimental method

2.1 Apparatus

A Hitachi Model 200-20 double beam spectrophotometer with 10 mm glass cell was used for the absorbance measurements.

All the pH measurements were done with a Toa Dempa pH meter, equipped with combined calomel and glass electrodes.

2.2 Reagents

Standard nickel solution, 10 ppm. Prepared by diluting 10 ml of 1000 ppm standard nickel solution(Analytical reagent grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan) to 1000 ml with water.

APDC solution, 0.2%. Prepared by dissolving 0.2 g of APDC in 100 ml of water.

Naphthalene solution, 20%. Prepared by dissolving 20 g of naphthalene in 100 ml of acetone.

Buffer solutions of different pH values were prepared by mixing 1M acetic acid and 1M ammonium acetate solution for pH 3-6, or 1M aqueous ammonia and 1M ammonium acetate solution for pH 8-11.

Deionized water was used.

The chemicals used were either chemically pure or reagent-grade materials unless otherwise mentioned.

2.3 Recommended procedure

Transfer about 45 ml of solution containing 1-9 ml of 10 ppm nickel solution to a tightly stoppered Erlenmeyer flask, adjust to pH 4.5 with 2.0 ml of the buffer solution and add 1.0 ml of 0.2% APDC solution. Mix the solution well and add 2.5 ml of 20% naphthalene solution. Then shake it vigorously for 1 min. Collect the colored naphthalene mixture on a funnel with disc-shaped filter plate(filter paper, No5C, Toyo Roshi Co., Ltd., Tokyo, Japan). Wash with water and dry in a dryer at about 60°C. Then dissolve in dimethylformamide and dilute to 10 ml. Measure the absorbance of the solution in 10 mm cell against the reagent blank prepared similarly.

3 Results and discussion

3.1 Absorption spectra

Figure 1 shows the absorption spectra of the reagent blank and the nickel APDC complex in naphthalene-dimethylformamide solution. The nickel complex has a absorption peak at 379 nm. The reagent blank shows strong absorption below 330 nm. Therefore, wavelength 379 nm was chosen for the absorbance measuerments.

3.2 Effect of pH

The effect of pH on the absorbance of the complex was investigated at 379 nm. The pH measurements were made after collection of the complex at room temperature. Figure 2 shows the effect of pH on the absorbance. It is evident that the absorbance is dependent of pH, the maximum absorbance being obtained between pH 1.2 and 10.2 and decreases on either side of these ranges. Therefore, a pH of the solution was adjusted 4.5 for the absorbance measurements

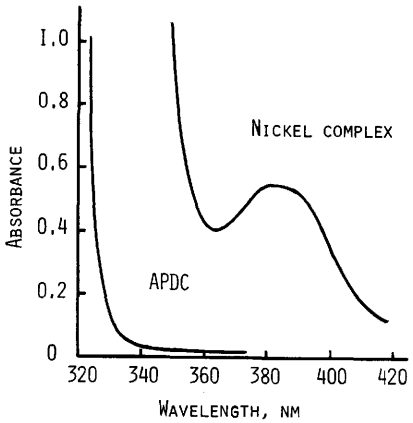

FIG. 1 ABSORPTION SPECTRA OF REAGENT AND NICKEL COMPLEX IN NAPHTHALENE-DMF SOLUTION
NICKEL : 50 μG ; PH : 4.5 ; 0.2% APDC : 1.0 ML ; 20% NAPHTHALENE : 2.5 ML ; SHAKING TIME : 1 MIN
REFERENCE : WATER

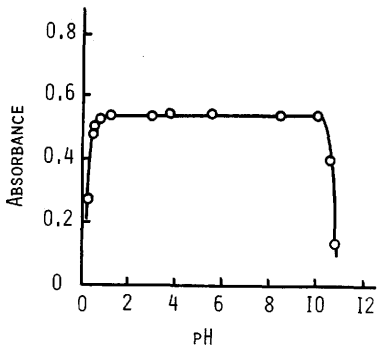

FIG. 2 EFFECT OF PH
NICKEL : 50 μG ; WAVELENGTH : 379 NM ; 0.2% APDC : 1.0 ML ; DIGESTION TIME : 15 MIN ; SHAKING TIME : 1 MIN
REFERENCE : REAGENT BLANK

3.3 Effect of APDC concentration

Varying volume of 0.2% APDC solution were added in the solution containing fixed nickel and buffer solution at pH 4.5, and the variation in the absorbance with the reagent concentration was investigated. The result is shown in Fig.3. The absorbance increased with increasing amount of this reagent up to 0.2 ml of 0.2% APDC solution and when 0.2-3.0 ml of this solution were used, the absorbance were reasonably constant. Therefore, 1.0 ml of 0.2% APDC solution were added for the absorbance measurements.

3.4 Effect of buffer solution and digestion time

The effect of the addition of the buffer solution on the absorbance was investigated. From the experimental result, the ab-

sorbance was no change by addition of the buffer solution up to 5.0 ml. Therefore, 2.0 ml of the buffer solution(pH 4.5) were added for the absorbance measurements.

The nickel complex in the solution containing 50 μg of nickel was digested between 2 and 50 min at room temperature, and the effect of digestion time on the absorbance was investigated. The variation in the absorbance was not seen for this period of digestion time. Therefore, 5 min of digestion time were selected for the absorbance measurements. The result is shown in Table 1.

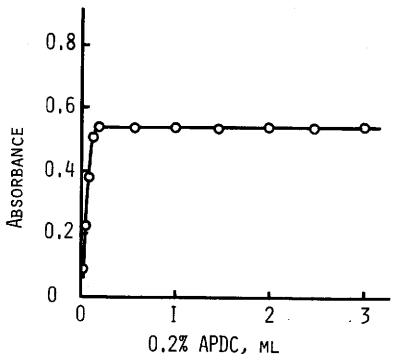

FIG. 3 EFFECT OF REAGENT CONCENTRATION
NICKEL : 50 μG ; WAVELENGTH : 379 NM ;
pH : 4.5 ; 20% NAPHTHALENE : 2.5 ML ;
REFERENCE : REAGENT BLANK

Table 1 Effect of digestion time

Digestion time min	Absorbance 379 nm
2	0.530
5	0.535
10	0.526
15	0.532
20	0.536
40	0.540
50	0.545

Nickel : 50 μg ; pH : 4.5 ;

3.5 Effect of naphthalene concentration

Various volume of 20% naphthalene acetone solution was added to the solution containing the nickel complex, and the effect of addition of naphthalene solution on the absorbance was examined. The result is shown in Table 2. The absorbance increased slightly up to 0.5 ml, and then was almost constant between 0.5 and 5.0 ml. Therefore, 2.5 ml of 20% naphthalene solution were added for the absorbance measurements.

Table 2 Effect of naphthalene concentration

20% naphthalene acetone ml	Absorbance 379 nm
0	0.500
0.2	0.516
0.5	0.533
1.0	0.537
1.5	0.530
2.0	0.540
3.0	0.538
4.0	0.533
5.0	0.538

Nickel : 50 μg ; pH : 4.5

3.6 Effect of shaking time

The effect of shaking time on the absorbance of the complex was examined. The result is shown in Table 3. The adsorption of the nickel complex on microcrystalline naphthalene was very fast and no change was seen in the degree of the adsorption when shaking time was varied up to 3.0 min. Therefore, 1 min of shaking time was selected for the absorbance measurements.

Table 3 Effect of shaking time

Shaking time sec	Absorbance 379 nm
0	0.500
10	0.537
20	0.534
40	0.540

60	0.544
90	0.540
120	0.550
180	0.544

Nickel : 50 μg ; pH : 4.5

3.7 Effect of standing time

The adsorbed mixture of the complex and naphthalene was separated from the aqueous solution, dried in a dryer and dissolved in dimethylformamide. The color of the complex in naphthalene-dimethylformamide solution was very stable for 40 min. Therefore, 10 min of standing time were chosen for the absorbance measurements.

Table 4 Effect of standing time

Standing time min	Absorbance 379 nm
5	0.542
10	0.540
15	0.540
20	0.539
30	0.542
40	0.542

Nickel : 50 μg ; pH : 4.5

3.8 Calibration curve for nickel

Based on the optimum conditions described above, the absorbances of the complex for nickel of various concentrations were measured at 379 nm against the reagent blank. The result is shown in Table 5. The absorbance of the complex showed a linear relationship to the concentration of nickel over the range 5-93 μg at 379 nm per 10 ml of dimethylformamide. The molar absorptivity was 6.34×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$ at 379 nm, the sensitivity being 9.26×10^{-3} $\mu g/cm^2$ of nickel at 379 nm for the absorbance of 0.001. The relative standard deviation was 0.62% at 379 nm.

3.9 Choice of solvent

The tests were made with various organic solvents to dissolve the mixture of nickel complex and naphthalene. The mixture is easily soluble in chloroform, acetonitrile, MIBK at room temperature, soluble

Table 5 Calibration data for nickel

Nickel concentration µg	Absorbance 379 nm
10	0.108
20	0.215
40	0.430
50	0.540
60	0.649
80	0.860
90	0.970

Wavelength : 379 nm ; pH :4.5

in propyrene carbonate and DMSO on warming, but insoluble in benzene, toluene, xylene and o-dichlorobenzene even on warming.